

What is claimed is:

1. A zinc-free glass frit comprising, by weight, from about 50% to about 70% SiO₂, from about 5% to about 20% CaO, from about 3% to about 15% Al₂O₃, up to about 20% BaO, up to about 15% B₂O₃, up to about 10% K₂O, up to about 6% Na₂O, up to about 10% ZrO₂, up to about 5% MgO and up to about 5% PbO.
2. The zinc-free glass frit according to claim 1 comprising, by weight, from about 52.0% to about 64% SiO₂, from about 8% to about 15% CaO, from about 4% to about 11% Al₂O₃, from about 7% to about 15% BaO, up to about 13% B₂O₃, from about 2% to about 8% K₂O, up to about 4% Na₂O, up to about 8% ZrO₂ and up to about 3% MgO.
3. The zinc-free glass frit according to claim 1 comprising, by weight, from about 53% to about 61% SiO₂, from about 10% to about 12% CaO, from about 5.5% to about 9% Al₂O₃, from about 8% to about 12% BaO, up to about 12% B₂O₃, from about 3.5% to about 6% K₂O, up to about 2% Na₂O, up to about 8% ZrO₂ and up to about 2% MgO.
4. A glaze composition for forming a glossy protective surface on ceramic architectural tile, the glaze composition comprising a zinc-free glass frit, the zinc-free glass frit comprising, by weight, from about 50% to about 70% SiO₂, from about 5% to about 20% CaO, from about 3% to about 15% Al₂O₃, up to about 20% BaO, up to about 15% B₂O₃, up to about 10% K₂O, up to about 6% Na₂O, up to about 10% ZrO₂, up to about 5% MgO and up to about 5% PbO.
5. The glaze composition according to claim 4 wherein the zinc-free glass frit comprises, by weight, from about 52% to about 64% SiO₂, from about 8% to about 15% CaO, from about 4% to about 11% Al₂O₃, from about 7% to about 15% BaO, up to about 13% B₂O₃, from about 2% to about 8% K₂O, up to about 4% Na₂O, up to about 8% ZrO₂ and up to about 3% MgO.

6. The glaze composition according to claim 4 wherein the zinc-free glass frit comprises, by weight, from about 53% to about 61% SiO₂, from about 10% to about 12% CaO, from about 5.5% to about 9% Al₂O₃, from about 8% to about 12% BaO, up to about 12% B₂O₃, from about 3.5% to about 6% K₂O, up to about 2% Na₂O, up to about 8% ZrO₂ and up to about 2% MgO.

7. A method of forming a protective glaze surface on an architectural tile comprising:

providing a ceramic body;

applying a glaze composition to the ceramic body, the glaze composition comprising a zinc-free glass frit comprising, by weight, from about 50% to about 70% SiO₂, from about 5% to about 20% CaO, from about 3% to about 15% Al₂O₃, up to about 20% BaO, up to about 15% B₂O₃, up to about 10% K₂O, up to about 6% Na₂O, up to about 10% ZrO₂, up to about 5% MgO and up to about 5% PbO; and

firing the ceramic body to fuse the glaze composition to a surface thereof.

8. The method according to claim 7 wherein the applied glaze composition and ceramic body are co-fired during a single fast firing cycle at a temperature of from about 1080°C to about 1180°C.

9. The method according to claim 7 wherein the glaze composition is applied to the ceramic body after the ceramic body has been once-fired, and wherein the applied glaze composition and the once-fired ceramic body are co-fired during a second firing in a double fast firing cycle at a temperature of from about 1000°C to about 1150°C.

10. The method according to claim 7 wherein the glaze composition and the ceramic body are co-fired in a *gres porcellanato* ceramic firing cycle at a temperature of from about 1160°C to about 1250°C.

11. The method according to claim 7 wherein:
the zinc-free glass frit comprises BaO;
an ink composition comprising Cr⁺³ ions is applied to the applied glaze
composition prior to firing; and
a yellow coloration develops in the protective glaze surface where the ink was
applied and fired.

12. The method according to claim 7 wherein:
the zinc-free glass frit comprises BaO;
a conventional ink composition for decorating ceramic products is applied to the
applied glaze composition prior to firing; and
a coloration develops in the protective glaze surface.